Coprocessing of Agricultural Plastic Waste and Switchgrass via Tail Gas Reactive Pyrolysis

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S Supporting Information

ABSTRACT: Pyrolysis of mixtures of agricultural plastic waste in the form of polyethylene hay bale covers (PE) (4−37%) and switchgrass were investigated using the US Department of Agriculture's tail gas reactive pyrolysis (TGRP) process at different temperatures (400−570 °C). TGRP of switchgrass and plastic mixtures significantly reduced the formation of waxy solids that are produced during regular pyrolysis. Under an atmosphere of approximately 70% recycled tail gas, mostly noncondensable gases were produced along with highly deoxygenated and aromaticized pyrolysis oil. When the atmosphere was diluted further to a recycled tail gas concentration of about 55%, higher yields of liquid product were achieved but with less deoxygenation. TGRP of low plastic mixtures (4−8%) produced oils with increased carbon and reduced oxygen content compared to the fast pyrolysis of switchgrass alone. Noncondensable gas fractions containing high concentrations of H_2, CO, ethylene, and other light hydrocarbons remained a significant portion of the product mixture at temperatures above 500 °C.

INTRODUCTION

Pyrolysis of biomass produces pyrolysis oils that are highly oxygenated and acidic.[1] Along with high water content and low higher heating values (HHV), these pyrolysis oils are also thermally unstable and over time or upon heating oligomerize to intractable higher molecular weight materials.[1] For these reasons, there have been substantial efforts toward production of stable deoxygenated pyrolysis oil through modification of the pyrolysis process. Catalytic pyrolysis of biomass in the presence of zeolites can alleviate these issues by producing pyrolysis oils that consist of more desirable aromatic hydrocarbons.[2] HZSM-5 is one of the most studied catalysts for the catalytic fast pyrolysis of biomass[3−10] and also has been shown to be one of the more effective catalyst for hydrocarbon production.[2,11] Recently it was found that pyrolysis oils with properties similar to those produced from the catalytic pyrolysis of switchgrass could be produced using tail-gas reactive pyrolysis (TGRP). TGRP is a patent-pending USDA-ARS process that relies on performing fluidized bed pyrolysis at carefully controlled reaction conditions under a non-inert atmosphere partially comprised of gas recycled from the tail stream. Use of the optimized conditions on lignocellulosic feedstocks enhances the deoxygenation of bio-oil toward oxygen concentrations comparable and/or better than that realized by catalytic fast pyrolysis via production of aromatic hydrocarbons without the use of an externally added catalyst.[12] Others have utilized atmospheres other than nitrogen[13−16] as well as actual recycled pyrolysis product gases[17−19] in an attempt to alter the final products from these thermochemical conversion processes. For both CFP and TGRP the low effective hydrogen-to-carbon ratio (H/C_{eff}),[4] characteristic of biomass, leads to inefficient biomass carbon conversion and produces a significant amount of CO, CO_2, polyaromatics, and coke that eventually causes catalyst deactivation.[2,20] Although TGRP alleviates the problem of catalyst deactivation, the achievable carbon yield is still limited by the low H/C ratio. The copyrolysis of biomass with a feedstock that has a higher H/C_{eff} ratio, such as plastics, has been shown to increase the production of hydrocarbons[21−26] while reducing the production of coke and char.[13−15] An increase in the production of hydrocarbons in the pyrolysis products of TGRP using a feedstock with a higher H/C_{eff} ratio has also been observed.[27] Plastics have been used as feedstocks for copyrolysis with biomass before and have been shown to produce olefins (mostly ethylene and propylene).[21,28] The incorporation of olefins as the fluidization gas in the catalytic pyrolysis of biomass has also been studied[13,29] and have shown to lead to a higher conversion of the biomass feedstock and a higher yield of aromatics.[13] In this study we looked to produce olefins *in situ* through thermal decomposition of plastic to produce pyrolysis oils, char, and gases using the TGRP process with agricultural plastic waste and switchgrass blends. The pyrolysis oils and product gases from the TGRP of switchgrass and agricultural plastic waste are compared to those produced from regular pyrolysis of the two feedstocks as well as to those from the regular pyrolysis and TGRP of switchgrass alone. The overarching objective was that if successful, then using agricultural plastic waste as a feedstock for copyrolysis of biomass could have the added benefit of providing a method for the conversion of a large amount agricultural plastic waste into value added products[30,31] via a process that is more environmentally friendly than incineration[32,33] and does not require the cost and work intensive cleaning necessary for recycling.[34,35] The goal of this study was to explore the plastic utilization in quantities that complement the TGRP process and establish the optimum coprocessing conditions in terms of ease of operation along with pyrolysis oil yield and quality.

Table 1. Feedstock Composition and Experimental Conditions for the Regular and Tail-Gas Reactive Pyrolysis (TGRP) of Agricultural Plastic (PE) and Switchgrass

experiment	1	2	3	4	5	6	7[a]	8[a]
wt % PE of mixture	37	16	16	16	8	4	0	0
total feedstock (kg)	2.57	2.73	2.74	2.70	2.78	2.85	~3.0	~3.0
feed rate (kg/h)	0.69	1.05	1.06	0.80	1.05	1.19	1.5	1.5
temperature (°C)	~540	500−570	400−450	420−540	480−550	520−540	450−500	450−500
pyrolysis	regular	TGRP	TGRP	TGRP	TGRP	TGRP	regular	TGRP
recycle gas (%)	N_2	54−76	42−76	42−69	44−70	42−58	N_2	65−80

[a]Experimental values taken from ref 12.

■ EXPERIMENTAL SECTION

Feedstock Preparation. Switchgrass was obtained from the McDonnell Farm (East Greenville, PA, USA), and polyethylene hay bale covers used to preserve undried hay were obtained from the Berks County Agricultural Center (Leesport, PA, USA). The hay bale covers were cleaned, ground, and sieved to a size of 2−8 mm by All Grind Plastics, Inc. (Asbury, NJ, USA). Elemental analysis using a Thermo EA1112 CHNS/O analyzer and flash pyrolysis experiments using a CDS 5250-T Pyroprobe with Autosampler (CDS Analytical, Oxford, PA) were conducted on samples of the hay bale covers and confirmed their identity as polyethylene (Tables S1−S2 and Figure S1) and will now be referred to as PE. Switchgrass was ground using a Wiley Mill No. 1 (Arthur H. Thomas Co., Philadelphia, PA, U.S.A.) and sieved to a size of 2 mm. Switchgrass and PE were dried overnight then combined in mixtures of 4%−37% PE by mass using a PK Liquid−Solids Blender No. LB-7889 (Patterson-Kelley Company, East Stroudsburg, PA) for 0.25 h. Elemental analysis and water and ash content of the switchgrass and plastic used for the regular and Tail Gas Reactive Pyrolysis (TGRP) experiments are given in Table S3.

Fast and Tail Gas Reactive Pyrolysis. Pyrolysis experiments were performed using the ERRC bubbling fluidized bed fast pyrolysis processes development unit (PDU).[12,36] The reactor bed consisted of a 7.6 cm diameter pipe filled to a depth of 20 cm of sand. Char removal is accomplished by cyclone separation, and pyrolysis liquids are collected at four stations in a condensation train connected in series followed by an electrostatic precipitator (ESP). For TGRP experiments, the PDU was equipped for operation on recycled product gas by including a regenerative blower with an inlet port connected to the ESP outlet to return ESP tail gases to the fluidized bed upon reheating through an electric heater. A remotely controlled gas outlet valve in the blower inlet line allows for the discharge of the preheated returned gases to maintain a constant system volume. A nitrogen feed (8−15 L/min) into the reactor was maintained during these experiments. The concentration of N_2 in the tail gas was monitored by micro GC and adjusted to the desired concentration by manipulation of the N_2 input rate. The feedstock composition and experimental conditions are given in Table 1. After a suite of experiments at varying process conditions were performed in order to optimize the conditions for production of deoxygenated bio-oil in high yield, the optimum conditions (experiment 5) found were duplicated to ensure reproducibility. All results from experiment 5 are an average of the duplicate experiments which had little variation.

Product Characterization. Elemental analysis (CHNS) was conducted using a Thermo EA1112 CHNS analyzer. The oxygen content was calculated by difference, and water content

was subtracted. Water content was determined using Karl Fischer titration in methanol with Hydranal Karl Fischer Composite 5 (Fluka) used as the titrant. Total acid number (TAN) was measured using a Mettler T70 automatic titrator with 0.1 M KOH in isopropyl alcohol used as a titrant and wet ethanol as the titration solvent. GC with mass spectroscopy (MS) detection analysis of pyrolysis oil was performed on a Shimadzu GCMS QC-2010. The column used was a DB-1701 at 60 m × 0.25 mm and 0.25 μm film thickness. The oven temperature was programmed to hold at 45 °C for 4 min, ramp at 3 °C/min to 280 °C, and hold at 280 °C for 20 min. The injector temperature was 250 °C, and the injector split ratio was set to 30:1. The flow rate of the He carrier gas was 1 mL/min. The pyrolysis oil samples for GC analysis were prepared as 3, 10, and 20 wt % (±1 wt %) solutions in acetone or methanol, which were filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter prior to injection. For quantification of individual pyrolysis oil compounds, response factors relative to the internal standard, fluoranthene, were determined using authentic compounds.[34] Noncondensable gas (NCG) composition was measured online using an Agilent 3000 MicroGC.

Product Yield Determination. Total mass closure for the regular pyrolysis experiment comprising agricultural plastic and switchgrass (Experiment 1) was 43%, with pyrolysis oil and a solid waxy material deposited throughout the system downstream of the fluidized bed accounting for most of the losses. Pyrolysis product yield distribution was determined gravimetrically and corrected for material imbalance caused by product deposition in the system by using a nonlinear programming optimization model.[28] The amount of pyrolysis oil, char, noncondensable gases, and water as a percent of input carbon, hydrogen, and oxygen for each of the TGRP experiments can be found in Figure S2.

Nuclear Magnetic Resonance Spectroscopy. Nuclear Magnetic Resonance Spectroscopy (NMR) was conducted on the oils from the regular and tail-gas reactive pyrolysis of agricultural plastic and switchgrass. Carbon 13 NMR (^{13}C NMR), Proton NMR (^{1}H NMR), and Distortionless Enhancement Polarization Tranfer (DEPT) spectra were obtained for each of the oils. Solution-state NMR spectra were recorded at 9.4 T on a Varian Inova NMR spectrometer (Palo Alto, CA) using a 5 mm dual broad-band probe equipped with z-axis pulsed field gradients or on a 14 T Agilent VNMRS NMR spectrometer (Santa Clara, CA) using a 5 mm One NMR probe with z-axis pulsed field gradients. All spectra were acquired at 40 °C in either CD_3OD or d_6-DMSO. The [1]H (proton) spectra, at 400 MHz, had a spectral width of 13 ppm and were acquired with a 45° pulse angle with a 6 s relaxation delay and were referenced to the sodium salt of 3-(trimethylsilyl)propionic acid-d_4 (TSP). All ^{13}C spectra had a sprectral width of 250 ppm, were acquired using a 45° pulse

angle, inverse-gating, and were referenced to the solvent ^{13}C peak. Reasonable signal-to-noise was achieved with 15,000−70,000 transients, utilizing a 4 or 6 s relaxation delay to provide adequate recovery of the signal for integration purposes. All data processing was performed using Spinworks4 (Version 4.1.0.0) (Copyright 2015, Kirk Marat, University of Manitoba (ftp://davinci.chem.umanitoba.ca/pub/marat/SpinWorks/). The ^{13}C and ^{1}H NMR spectra were integrated and used to quantify carbon atoms and proton atoms in the pyrolysis oils. This information was then used to determine the percentage of carbons and protons in different chemical functional groups based on the chemical shift.

RESULTS AND DISCUSSION

Pyrolysis Product Yields and Composition. The study began with pyrolyzing a blend of 37 wt % polyethylene hay bale covers and 63 wt % switchgrass at 540 °C under an inert (N_2) atmosphere (experiment 1). Although optimum thermal breakdown of polyethylene occurred above 550 °C for fast pyrolysis,[37] we chose the slightly lower temperature with the hope to increase the conversion of biomass and plastic to high quality pyrolysis oil and avoid converting the feedstocks to gas. However, this resulted in a large amount of partially depolymerized polyethylene solids and waxes being deposited within the collection system of the pyrolysis unit (Figure 1, A-

Figure 1. Images of soft brown waxy solid material collected in the first electrostatic precipitator (ESP) (A) and the funnel of the first ESP (B) after the regular pyrolysis of agricultural plastic (PE) and switchgrass. Images of a thin film of oil collected in the first ESP (C) and the relatively clean funnel of the first ESP after the tail-gas reactive pyrolysis (TGRP) of PE and switchgrass.

B). This challenge made performing a complete mass balance impractical thereby advising subsequent operating temperatures and feedstock blends. Compared with switchgrass alone, the gases produced from this blend (Table 2) consisted of more H_2 and light hydrocarbons and lesser concentrations of CO and CO_2. This suggested that the more reactive gas produced from the pyrolysis of the blend as compared with biomass alone could influence TGRP. This challenge, along with our previous experience in effectively using TGRP for depolymerizing high molecular weight plant resins and rubber such as guayule,[27] advised that perhaps the TGRP process could be better suited for the copyrolysis of switchgrass/polyethylene blends.

The first TGRP run was therefore carried out at a lower plastic blend rate than the initial fast pyrolysis experiment to minimize the amount of waxy solids produced in the system. The TGRP recycle gas rate was also set at 70% (experiment 2), a condition at which experiments involving biomass alone are optimum.[12] While the TGRP was successful in preventing the formation of waxy solids in the system (Figure 1, C−D), even when a temperature lower than what is usually necessary for the complete degradation of polyethylene was utilized, these conditions also led to a high noncondensable gas yield (64%) (Figure 2) at the expense of liquid. The gas produced exhibited high concentrations of hydrogen (~30 mol %) and CO (~40 mol %) with the balance comprising of mostly light hydrocarbons such as ethylene (5.5 mol %) and only a small fraction of CO_2 leading to a gas with high calorific value of about 21.8 MJ/kg. The accompanying pyrolysis oil had very low oxygen content and TAN, the lowest among the TGRP oils produced in all the experiments (Table 3). The oil was also highly aromatized as evident by its low H/C molar ratio and higher concentration of mostly polyaromatic hydrocarbons (PAH) and naphthalenes (Table 4). ^{1}H and ^{13}C NMR analyses confirmed these observations by showing that 92% of the proton signals and all of the observable carbon signals from the oil were associated with aromatic compounds (Tables S4 and S5). In this case the water yield was high, but this aqueous fraction contained very little dissolved carbon (Table 4).

In an effort to reduce the gasification of the feedstock blend and the over aromatization of the pyrolysis oil, the returned tail gas for the TGRP process was further diluted with nitrogen (from 70% to 59% recycled gas content). The reactor temperature was also reduced from 500 °C to the 400−450 °C range (experiment 3). These conditions resulted in a decreased gas yield and an increase in the associated pyrolysis oil and char produced (Figure 2). The fuel quality of the gas fraction was reduced when compared with experiment 2, with the concentration of CO_2 increasing to over 20 mol % and the fraction of hydrogen reduced to 5.8 mol %. In this case, the oil produced had the highest oxygen content among the TGRP experiments (Table 3) contributed by the presence of oxygenates such acetic acid, acetol, levoglucosan, phenol, and cresols in the oil (Table 4). The high concentrations of levoglucosan and other oxygenates in the oil and aqueous fractions from experiment 3 along with the increased TAN value give indication that deoxygenation of biomass was not realized under these TGRP conditions as previously observed,[12] possibly due to the lower operational temperature employed. Unlike the other TGRP experiments, NMR shows that experiment 3 yielded significant amounts of protons associated with alkanes (31.4%) and carbons associated with aliphatic (22.1%) compounds (Tables S4 and S5, respectively).

The high char yield and increased oxygen concentrations in the oil from experiment 3 led us to try a higher temperature (420−540 °C) while maintaining a similar recycled gas concentration (avg 56% recycled gas in the atmosphere) for experiment 4. For this set of conditions, the noncondensable gas yield increased compared to experiment 3 and the char production decreased significantly. Experiment 4 yielded the highest pyrolysis oil amounts among the TGRP experiments (Figure 2) with a better fuel quality gas comprising higher concentrations of H_2 and C_2H_4 and lower concentrations of CO_2 than that produced at the comparable but lower temperature experiment 3. The pyrolysis oil produced in this case was deoxygenated and aromatized but less so in

Table 2. Composition of Product Gases (mol %, N_2 Free) from the Regular and Tail-Gas Reactive Pyrolysis (TGRP) of Agricultural Plastic (PE) and Switchgrass (SWG)

experiment	1	2	3	4	5	6	7[a]	8
H_2	11.1	29.2	5.8	10.7	13.4	17.2	5.1	6.6
CH_4	13.9	17.1	14.2	16.9	16.9	14.5	7.8	13.8
CO	45.6	39.7	47.4	47.6	48.0	47.5	57.6	52.0
CO_2	5.0	8.2	21.7	12.5	11.3	12.6	29.5	20.7
C_2H_4	17.4	5.5	6.7	8.5	8.0	6.3	0	3.7
C_2H_6	0.7	0.2	2.0	1.9	1.2	0.9	0	1.8
C_3H_8	6.3	0.1	2.3	2.0	1.2	1.1	0	1.3
HHV^b (MJ/kg)	26.9	21.8	15.8	19.9	19.7	18.3	8.1	14.1

[a]Experimental values taken from ref 12. [b]Higher heating value was calculated from the composition of the product gases as a weighted sum of the gross heating value of the components.
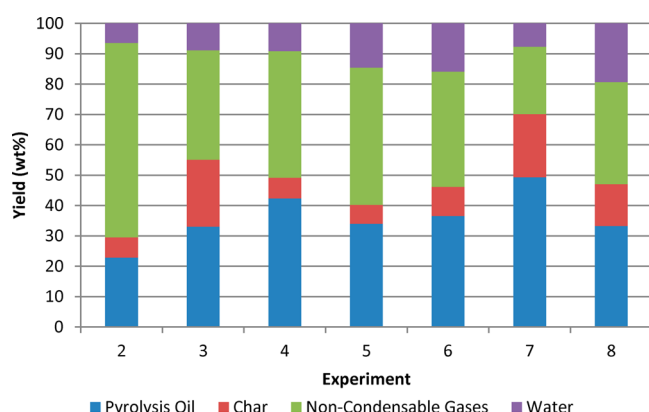
Figure 2. Yield distribution of products from the regular and tail-gas reactive pyrolysis (TGRP) of agricultural plastic (PE) and switchgrass. Numbers beneath each bar refer to the experiment number (see Table 1).

comparison to that produced in experiment 2 where the highest recycle gas rate of 70% was applied. The oxygen content in this case was ∼15 wt %, TAN was 33.6 mg KOH/g, and the H/C ratio was 0.8. The pyrolysis oil produced under experiment 4 had similar concentrations of naphthalene and polyaromatic hydrocarbons to that from experiment 2 but had an increased concentration of BTX compounds (Table 4). Based on the NMR analysis the major difference between the oil produced under the conditions in experiment 2 and experiment 4 was an increased percentage of protons alpha to an unsaturation (mostly aromatics) or heteroatom found in the oil from experiment 4 (Table S4). The yield of water produced was similar to that of experiment 2, but the aqueous phase did

contain more dissolved organics including acetic acid and levoglucosan.

Having established that the conditions under experiment 4 yielded the desired TGRP results we set out to optimize the plastic blend. The amount of plastic in the feedstock mixture was further reduced (8 and 4 wt %) to determine the minimum amount of plastic necessary to obtain a positive effect on the oil composition (Experiments 5 and 6, respectively). In doing so, the amount of noncondensable gases produced increased and the amount of oil produced decreased compared to experiment 4 (Figure 2), but that is likely also attributable to the higher pyrolysis temperature used (>480 °C). Little difference in product distribution was noted between the 8 or 4 wt % plastic loading. The composition of the noncondensable gases produced were very similar to those in experiment 4 even though much less plastic was utilized in the feedstock mixtures (Table 2). While we were able to reproduce similar oil composition encountered in experiment 4 the oxygen content and TAN values trended slightly higher with decreasing plastic blend rates (Table 3). The increased oxygen content is attributable to increased concentration of phenol and cresols in the oil and decreased concentration of aromatic hydrocarbons (Table 4). This is confirmed by the ^{1}H NMR analysis where there were considerable more protons associated with either alcohol or methoxy compounds in the oil from experiments 5 and 6 compared to the oil from experiment 4 (Table S4).

Insight into the effects the various TGRP process conditions and loading of the plastic in the biomass blends on the pyrolysis chemical pathways and the composition of the resulting pyrolysis oils can be gained by some empirical observations. Figure 3 shows that there is a strong positive correlation (R^2 = 0.98) between the concentration of CO_2 in the produced gas

Table 3. Water Content, Elemental Analysis, Total Acid Number (TAN), and Energy Content (HHV) of Oil Produced from the Regular and Tail-Gas Reactive Pyrolysis (TGRP) of Agricultural Plastic (PE) and Switchgrass

experiment	1	2	3	4	5	6	7[a]	8[a]
water (wt %)	4.3	0.5	5.3	1.6	6.4	4.4	6.7	3.2
C (wt %, db)	72.2	87.7	63.0	78.1	78.4	68.2	59.8	80.3
H (wt %, db)	9.4	4.9	7.2	5.5	5.6	5.4	6.0	5.7
N (wt %, db)	0.5	0.4	0.6	0.8	1.5	1.4	0.9	1.5
O (wt %, db)[b]	17.9	7.1	29.2	15.6	19.4	25.0	33.3	12.5
C/O (mol)	5.4	16.6	3.2	6.7	5.4	3.6	2.0	8.5
H/C (mol)	1.6	0.7	1.8	0.8	0.9	1.0	1.2	0.8
TAN (mg KOH/g)[c]	68.2	16.4	54.0	33.6	52.3	79.3	119.0	24.0
HHV (MJ/kg, db)	26.3	39.4	28.7	36.4	34.0	31.6	23.4	33.2

[a]Values taken from ref 12. [b]Oxygen determined by difference. [c]Titration end point average.

Table 4. Concentration of Selected Compounds (GC/MS, wt%) from the Oil and Aqueous Fractions from the Regular Pyrolysis and Tail-Gas Reactive Pyrolysis (TGRP) of Switchgrass and Agricultural Plastic (PE)

experiment	1	2	3	4	5	6	7[a]	8[a]
oil phase								
acetic acid	6.2	trace	3.0	0.2	0.6	0.4	6.4	0.3
acetol	3.5	trace	1.1	0.1	0.1	0.2	5.6	nd[e]
levoglucosan	2.1	trace	5.1	trace	0.4	1.2	4.5	nd[e]
phenol	1.1	0.2	1.3	0.9	1.8	1.4	0.5	3.8
o,m-,p-cresols	1.0	0.1	1.5	0.8	1.8	3.1	0.6	2.5
BTX[b]	trace	0.3	trace	0.5	0.3	0.3	0.1	4.1
styrene	trace	0.8	0.3	0.7	0.5	0.9	NR	NR
selected naphthalenes[c]	0.1	7.7	1.4	6.3	3.1	1.9	nd[e]	5.4
selected PAHs[d]	0.1	4.8	0.8	4.3	2.0	4.7	NR	0.8
aqueous phase								
acetic acid	6.1	0.0	4.3	5.5	5.1	3.1	7.8	1.1
acetol	3.2	0.0	1.7	3.8	0.9	0.9	10.4	0.7
levoglucosan	0.3	0.0	5.1	4.0	0.3	0.1	1.7	nd[e]
phenol	1.2	0.3	0.1	1.3	0.6	0.4	nd[e]	nd[e]
cresols[b]	1.1	0.0	0.2	0.3	0.2	0.1	nd[e]	nd[e]
water	4.9	97.6	22.9	34.0	76.8	80.2	27	84.9

[a]Values taken from ref 12. [b]Benzene, toluene, o- and p-xylene. [c]Naphthalene, 1-methyl- and 2-methylnaphthalene. [d]Indene, biphenyl, fluorene, and anthracene. [e]nd = not detected.
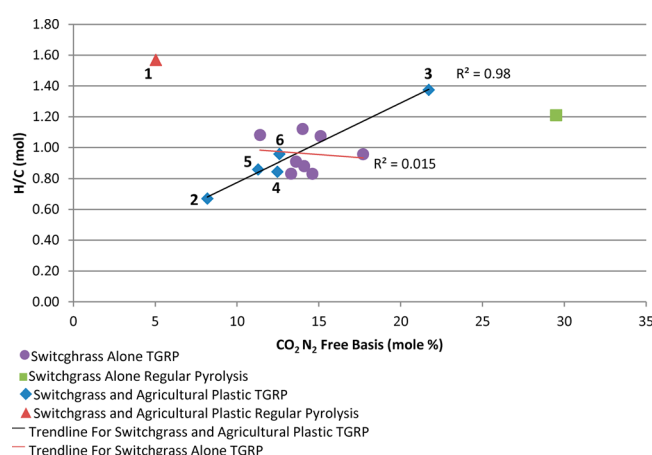
Figure 3. Comparison of CO_2 production to the H/C molar ratio of electrostatic precipitator (ESP) oils from the regular and tail-gas reactive pyrolysis (TGRP) of switchgrass and agricultural plastic (PE). Data point labels refer to experiment number (see Table 1).

and the H/C molar ratio of pyrolysis oils produced suggesting that as the biomass carbon is converted to CO_2 and the hydrogen rich plastic derivatives are more concentrated in the oil but not aromatized. It has been previously shown in the case of CFP that plastic derived carbon does not serve as a reducing agent, and any CO or CO_2 produced during copyrolysis is derived directly from biomass.[26] Furthermore, for TGRP of switchgrass alone, there is no trend between H content of the pyrolysis oil and production of CO_2 ($R^2 = 0.015$). We also observed that as the H_2 concentration in the produced gas increases the amount of oxygen in the bio-oil decreases as shown Figure 4. This relationship between H_2 and the extent of deoxygenation of the produced oils shows that copyrolysis of biomass and plastic is concurrent with aromatization where a reactive atmosphere is fueled by the produced gas. Taking the above observations together suggests that blending polyethylene with biomass does not result in synergistic hydrogen incorporation to liquid range products. Rather net deoxygenation is maximized by hydrogen loss to H_2 (and high gas yield),
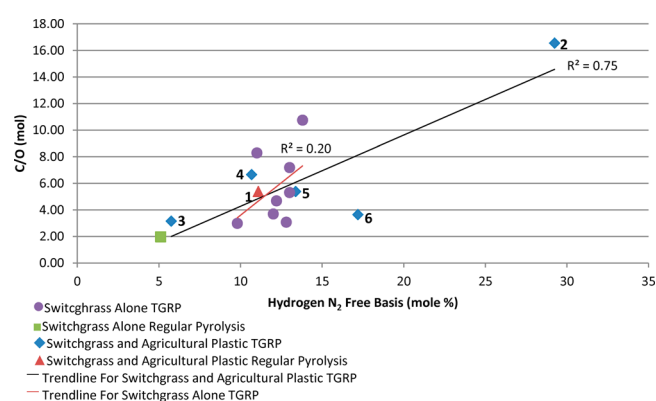
Figure 4. Comparison of H_2 concentration to the C/O molar ratio of pyrolysis oils from the regular and tail-gas reactive pyrolysis (TGRP) of switchgrass and agricultural plastic (PE). Data point labels refer to the experiment number (see Table 1).

and maximum plastic derived hydrogen incorporation is maximized by conditions that do not favor the deoxygenation of the biomass derived species. However, using intermediate conditions, such as those used in experiments 4, 5, and 6 it was still possible to produce partially deoxygenated pyrolysis oils from switchgrass blended with 4−16 wt % agricultural plastics in yields of 35−40 wt %. These oils exhibit significantly improved properties compared with those from traditional fast pyrolysis of switchgrass and other biomass alone.

■ CONCLUSIONS

The co-TGRP based processing of switchgrass and polyethylene hay bale covers was studied. Under inert fast pyrolysis conditions, the polyethylene was unable to be completely depolymerized at temperatures near 550 °C, interrupting the process with waxy solid deposits formed throughout the system. Using the TGRP process conditions alleviated the formation of these solids, but achieving processes conditions that produced high yields of deoxygenated pyrolysis oils was elusive. When blends containing up to 16 wt % PE were

subjected to TGRP at temperatures ranging from 400 to 570 °C with 70% recycled product gases, noncondensable gases were the major product. This gas was rich in H_2, CO, ethylene, and other light hydrocarbons indicating a fuel rich reactive atmosphere for the copyrolysis resulting in the production of highly deoxygened and aromatic oil but in low yield. Copyrolysis oil yields could be increased at lower tail gas recycle rates at the expense of some oil quality (less deoxygenated) but still of significantly increased quality compared with traditional biomass pyrolysis oils. Partially deoxygenated pyrolysis oils could be produced with blends containing 4 to 16 wt % polyethylene. The data suggests that H_2 releasing aromatization is the driving force for deoxygenation, meaning enhancing the conversion of biomass to deoxygenated liquids by hydrogen transfer from polyethylene is not a major pathway operating in this process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b02597.

Qualitative analysis of the hay bale covers and ^{13}C and ^1H NMR spectra of the oils in this study (PDF)

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Notes
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